

## Synthesis and Rearrangements of 5-(1,2,3,4,5-Pentaphenylcyclopentadienyl)-isosenocyanate

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Unlike 5-(1,2,3,4,5-pentaphenylcyclopentadienyl)isothiocyanate, its selenium analogue 5-(1,2,3,4,5-pentaphenylcyclopentadienyl)isosenocyanate exists in solution in an equilibrium with the isomeric selenocyanate, both isomers being found to undergo circumambulatory rearrangements.

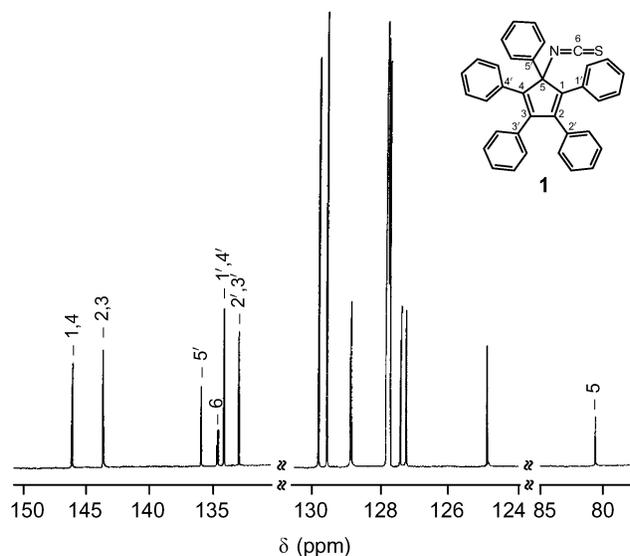
By treatment of 5-bromo-1,2,3,4,5-pentaphenylcyclopentadiene with potassium thio- or selenocyanate in acetonitrile solution (48 h, 24 °C) 5-(1,2,3,4,5-pentaphenylcyclopentadienyl)isothiocyanate **1**<sup>†</sup> and isosenocyanate **2**,<sup>†</sup> respectively, have been obtained as stable crystal compounds in almost quantitative yield. No thiocyanate and selenocyanate isomers **3**, **4** have been isolated.

The structure of compounds **1**, **2** has been proved by IR, <sup>13</sup>C NMR and mass spectral studies. In IR spectra of the compound **1** a broad absorption peak characteristic of the –N=C=S valence vibration region<sup>1</sup> was observed at 2080 cm<sup>-1</sup>, in both crystal and solution. In the <sup>13</sup>C NMR spectrum (75.47 MHz) of **1** in CDCl<sub>3</sub> (Fig. 1), the isothiocyanate carbon atom signal is found in its characteristic region (131–134 ppm)<sup>2</sup> at δ 134.52.

<sup>†</sup> **Compound 1**: yellow crystals (from acetonitrile), m.p. 198–199 °C, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.82–7.38 (25H, m, aromatic H). IR (Nujol) ν/cm<sup>-1</sup> 2080 (N=C=S); 1610, 1580 (C=C); 1480, 1180, 1150, 1070, 1030, 920. MS *m/z* 503 (100%) [C<sub>5</sub>Ph<sub>5</sub>NCS]<sup>+</sup> = [M]<sup>+</sup>, 471 (0.7) [M–S]<sup>+</sup>, 459 (0.5) [M–CS]<sup>+</sup>, 445 (91.1) [M–NCS]<sup>+</sup>.

**Compound 2**: yellow crystals (from acetonitrile), m.p. 188–189 °C, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.80–7.37 (25 H, m, aromatic H). IR (Nujol) ν/cm<sup>-1</sup> 1950 (N=C=S); 1615, 1590 (C=C); 1490, 1160, 1150, 1040, 980. MS *m/z* 548 (3.0) [C<sub>5</sub>Ph<sub>5</sub>NCSe]<sup>+</sup> = [M]<sup>+</sup>, 522 (1.5) [C<sub>5</sub>Ph<sub>5</sub>SeCN–CN]<sup>+</sup>, 471 (12.1) [M–Se]<sup>+</sup>, 459 (1.0) [M–CSe]<sup>+</sup>, 445 (100) [M–NCSe]<sup>+</sup>.

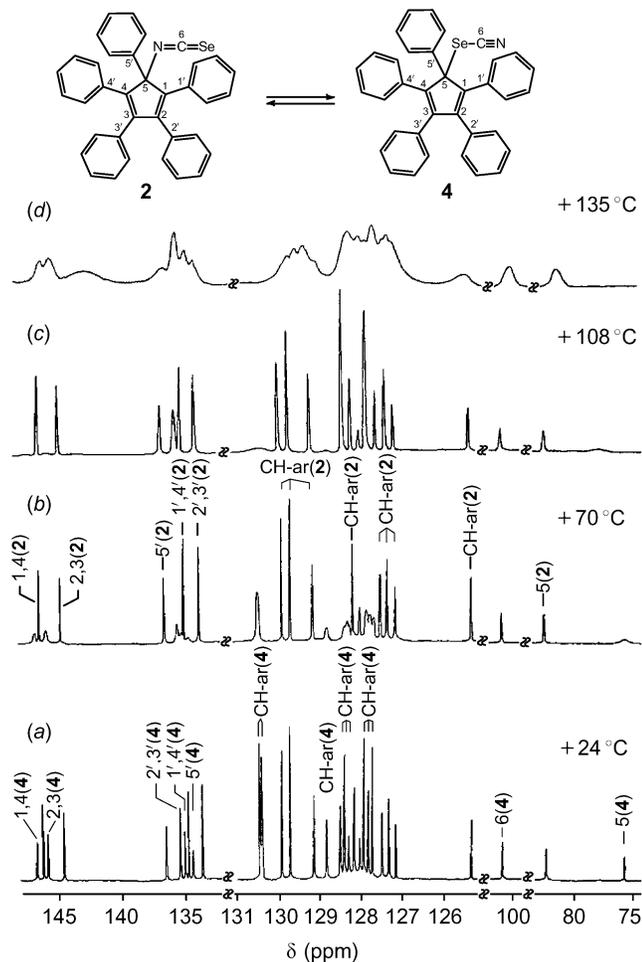
Compounds **1**, **2** gave satisfactory elemental analyses.



**Fig. 1** <sup>13</sup>C NMR (75.47 MHz) spectrum of compound **1** in CDCl<sub>3</sub>.

It is worth noting that the previously described reaction of lithium 1,2,3,4,5-pentamethylcyclopentadienide with dirhodane also resulted in the isothiocyanate derivative.<sup>3</sup> The IR

spectrum of compound **2** in the crystal also contains a broad intense absorption at  $1950\text{ cm}^{-1}$  relating to the valence vibration of the  $\text{-N=C=Se}$  group. However, in solution ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ) an additional weaker absorption at  $2150\text{ cm}^{-1}$  appears, which can be assigned to the  $\text{-Se-C}\equiv\text{N}$  group. This fact witnesses the existence of the  $\mathbf{2} \rightleftharpoons \mathbf{4}$  equilibrium in solution. This is confirmed by the  $^{13}\text{C}$  NMR spectrum of **2** (Fig. 2) which displays the presence of signals belonging to both isoselenocyanate **2** and selenocyanate **4** isomeric structures in the equilibrium ratio 3:2 ( $\text{CDCl}_3$ ) and 2:3 ( $\text{C}_6\text{D}_5\text{CD}_3$ ).<sup>‡</sup>



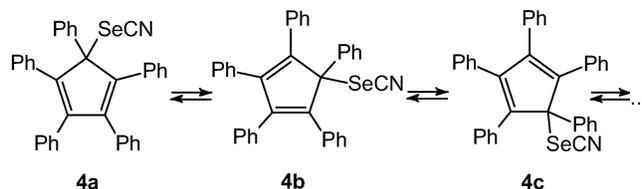
**Fig. 2**  $^{13}\text{C}$  NMR (75.47 MHz) (a)–(c) and (20.11 MHz) (d) spectra of the equilibrium mixture of compounds **2**, **4** in  $[\text{D}_8]\text{toluene}$  at (a)  $+25^\circ\text{C}$ , (b)  $+70^\circ\text{C}$ , (c)  $+108^\circ\text{C}$ , (d)  $+135^\circ\text{C}$  (under pressure). The solvent signals are excluded from the spectra.

Whereas isothiocyanate **1** exhibits no fluxional behaviour in solution at temperatures up to  $100^\circ\text{C}$ , the equilibrium mixture of its selenium analogues **2**, **4** reveals temperature dependent  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra over the temperature range  $24\text{--}135^\circ\text{C}$ . As Fig. 2 shows, the  $^{13}\text{C}$  signals of the

<sup>‡</sup> Assignment of the signals in the  $^{13}\text{C}$  NMR spectra was based on the characteristic values and intensities of carbon chemical shifts,<sup>4</sup> mono-resonance  $^{13}\text{C}$  NMR spectra and application of the APT technique. Signals of the  $\text{sp}^3$ -hybridised  $\text{C}^5$ -carbon atoms were found at  $\delta$ : 81.45 (**2**,  $\text{CDCl}_3$ ), 82.09 (**2**,  $\text{C}_6\text{D}_5\text{CD}_3$ ) and 75.65 (**4**,  $\text{CDCl}_3$ ), 75.73 (**4**,  $\text{C}_6\text{D}_5\text{CD}_3$ ). The low-field shift of the  $\text{C}^5$  signal in **2** is due to the anisotropic effect of the isoselenocyanate substituent ( $\alpha$ -effect).<sup>5</sup>

pentaphenylcyclopentadienyl moiety<sup>§</sup> of **4** become broadened at  $40\text{--}60^\circ\text{C}$  and coalesce at  $60\text{--}135^\circ\text{C}$ , the half-width of the  $\text{-SeCN}$  carbon signal remaining constant up to  $80^\circ\text{C}$  and broadening only on raising the temperature to  $135^\circ\text{C}$ . All the carbon signals of isomer **2** display temperature dependent behaviour similar to that of the  $\text{-SeCN}$  carbon signal of **4**, i.e. a reversible broadening of the signals on increasing the temperature of the solution from  $80$  to  $135^\circ\text{C}$ . Accounting for the regularities in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of fluxional cyclopentadienes prone to circumambulatory migrations of substituents in the ring, such a spectral behaviour of compounds **2**, **4** may be related to the following dynamic processes.<sup>¶</sup>

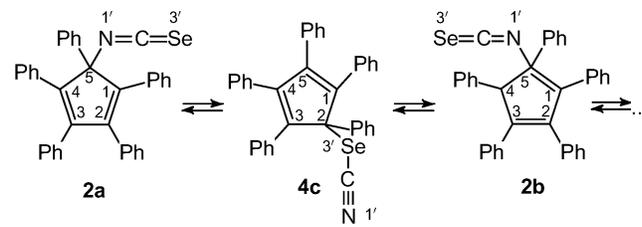
(i) Fast degenerate 1,5-sigmatropic shifts of the selenocyanate group along the perimeter of the cyclopentadiene ring of **4** (Scheme 1).



**Scheme 1**

From line shape analysis of the  $^{13}\text{C}$  NMR spectra, the following kinetic and activation parameters of the  $\mathbf{4a} \rightleftharpoons \mathbf{4b} \rightleftharpoons \mathbf{4c} \rightleftharpoons \dots$  rearrangements ( $[\text{D}_8]\text{toluene}$ ) have been calculated:  $\Delta G_{298}^\ddagger$  16.7 kcal mol<sup>-1</sup>,  $\Delta H^\ddagger$   $14.2 \pm 0.3$  kcal mol<sup>-1</sup>,  $\Delta S^\ddagger$   $-8.4 \pm 0.4$  e.u.,  $k_{298}$  3.4 s<sup>-1</sup>. These are close in value to those of degenerate migrations of other selenium-centred substituents in the cyclopentadiene ring.<sup>6,7</sup>

(ii) Slow ( $\Delta G_{408}^\ddagger \sim 22$  kcal mol<sup>-1</sup>) non-degenerate 3,3-hetero-Cope rearrangements  $\mathbf{2} \rightleftharpoons \mathbf{4}$  (Scheme 2).



**Scheme 2**

Such a mechanism was suggested for the migration of the isothiocyanate group around a seven-membered cycloheptatriene ring.<sup>5</sup> The 3,3-*N,N*- and *S,S*-stereo-Cope rearrangements in the cyclopentadiene ring have been reported earlier.<sup>8,9</sup>

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<sup>§</sup> The compounds **2**, **4** possessing  $\text{C}_s$ -symmetry have five groups of indicator signals (two groups of quaternary carbons of cyclopentadiene and aromatic rings, and three groups of aromatic carbons CH; the ratio of intensities in each group 2:2:1). Under a fast degenerate *i,j*-sigmatropic shift, these signals are reversibly broadened and coalesce in each group forming five common signals, the migrant signal being unaffected by the above exchange. Under non-degenerate *i,j*-hetero-Cope rearrangement in the cyclopentadiene ring, the spectral behaviour of the cyclopentadiene moiety is similar to the above; however, the migrant signals are broadened simultaneously with the other indicator signals and then coalesce between each other.

<sup>¶</sup> The evolution of the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of compounds **2**, **4** does not depend on the solution concentration ( $0.05\text{--}0.5\text{ mol dm}^{-3}$ ).

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